NASA TECHNICAL MEMORANDUM

NASA TM X-68011

NASA TM X-68011

ADDITION-TYPE POLYIMIDES FROM SOLUTIONS OF MONOMERIC REACTANTS

by P. Delvigs, T. T. Serafini,
and G. R. Lightsey
Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER proposed for presentation at
Seventeenth National Symposium of the Society of
Aerospace Material and Process Engineers
Los Angeles, California, April 11-13, 1972

ADDITION-TYPE POLYIMIDES FROM SOLUTIONS OF MONOMERIC REACTANTS

P. Delvigs, T. T. Serafini, and G. R. Lightsey
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

Abstract

The monomeric reactants approach was used to fabricate addition-type polyimide/graphite fiber composites with improved mechanical properties and thermal stability characteristics over those of composites derived from addition-type amide acid prepolymers. A screening study of 24 different monomer combinations was performed. The results of a more extensive investigation of a selected number of monomer combinations showed that the combination providing the best thermomechanical properties was 5-norbornene-2,3-dicarboxylic acid monomethyl ester/4,4'-methylenedianiline/3,3'4,4'-benzophenonetetracarboxylic acid dimethyl ester at a molar ratio of 2/3.09/2.09.

E-6750

1. INTRODUCTION

One of the recent breakthroughs in the chemistry of high temperature resins was the development of a novel class of polyimides which cure by an addition reaction.[1,2] This approach uses low molecular weight amide acid prepolymers endcapped with reactive alicyclic rings that polymerize into thermally stable polyimides without the evolution of byproducts. A commercially available resin of this type is P13N. Another version, known as P10P, having considerably improved thermooxidative stability, has been developed.[3] From our in-house studies of matrix resins, we have observed that P10P prepolymer solutions exhibit a very limited shelf life at room temperature, as evidenced by precipitation or gel formation. Prior to the appearance of a precipitate or gel there is a steady decrease of solution viscosity.

To circumvent these limitations, we have demonstrated that it is not necessary to synthesize end-capped amide acid prepolymers. Instead, graphite fibers are impregnated with solutions of appropriate monomers, and the endcapped prepolymer is formed in situ by application of heat.[4] Solutions of monomeric reactants offer several advantages over amide acid prepolymer solutions, including excellent shelf life, increased solids loading, and lower viscosity. In addition, relatively non-toxic low-boiling alcoholic solvents such as methanol can be used as solvents for the monomers.

The purpose of the present study was, by using the monomeric reactants approach, to fabricate polyimide/graphite fiber composites with improved mechanical properties and thermal stability characteristics over those of P10P/graphite composites.

This report describes a screening study of 24 polyimide/graphite fiber composites [1.27 by 6.35 cm (1/2 by 2-1/2 in.)] fabricated from monomeric solutions differing in chemical composition or stoichiometry. The combination of monomers used for preparing the prepreg solutions was: (a) the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid; (b) the dimethyl ester of pyromellitic acid or 3,3'4,4'-benzophenonetetracarboxylic acid; and (c) an aromatic diamine.

Based on the screening study results, 7.62 by 25.4 centimeters (3 by 10 in.) composites were fabricated from several selected monomer solutions, and their mechanical properties and thermal stability characteristics determined at 315° C (600° F) over a period of 600 hours.

2. EXPERIMENTAL PROCEDURE

2.1 MONOMERS

The monomers used in this study are shown in table I. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) was prepared according to the method of Walton.[5] 2,5-Dicarbomethoxyterephthalic acid (PMDE) was prepared according to Bell and Jewell.[6]

The dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) was synthesized by refluxing a suspension of 3,3'4,4'-benzophenonetetracarboxylic dianhydride (96.6 g, 3.00×10^{-1} mole) in anhydrous methanol (95 ml) until the solid had dissolved (2 to 3 hr), then for an additional hour. Excess methanol was distilled off under reduced pressure at 50° C. The brownish oil was dried further in vacuum (10^{-3} torr) at room temperature for 24 hours to give 115.2 g (99 percent yield) of the isomer mixture BTDE as a crystalline solid. The solid crystals are hygroscopic, and were therefore stored in a sealed container under nitrogen.

4,4'-Methylenedianiline (MDA), 4,4'-oxydianiline (ODA), 4,4'-thiodianiline (TDA), and 4,4'-sulfonyldianiline (SDA) were obtained from a commercial source and recrystallized from 2-propanol.

p-Phenylenediamine (PPDA) and m-phenylenediamine (MPDA) were used as received.

Benzidine (BZD) was prepared from its dihydrochloride salt by treatment with dilute aqueous KOH. The crude BZD was recrystallized from a mixture of water and acetone (2:1 by volume).

4,4'-Diaminostilbene (DAS) was prepared from its dihydrochloride salt by treatment with dilute aqueous KOH. The crude DAS was recrystallized from 95 percent ethanol.

2.2 PREPREG SOLUTIONS

The solvent used was anhydrous methanol unless otherwise indicated (tables II and III). The solutions were prepared at a solids loading of 50 weight percent. The stoichiometry of the reactants was governed by the desired number of imide rings or by the desired percentage of alicyclic content.

2.3 COMPOSITE FABRICATION AND TESTING

Prepreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the various solutions of monomeric reactants to yield prepregs that contained 40 percent monomers and 60 percent fiber by weight. The prepregs made from monomer solutions in methanol were heated on the drum for 2 hours at 50° C (122° F) to reduce the solvent content to less than 10 percent by weight. The prepregs made from monomer solutions in 1-methyl-2-pyrrolidinone were heated for 2 hours at 50° C (122° F) and then for 10 minutes at 120° C (248° F) to effect a similar solvent content reduction. After this treatment, the prepreg tapes were flexible, but not tacky.

Unidirectional composites were molded essentially according to the method of Burns, et al.[3] Twelve plys of prepreg 1.27 by 6.35 centimeters (1/2 by 2-1/2 in.) were stacked between aluminum foil and heated for 2 to 4 hours in a 205° C (400° F) oven. The imidized prepregs were then placed in a mold preheated to 315° C (600° F). The mold was closed, contact pressure (dwell time) was applied for 30 to 50 seconds, and then a pressure of 6.24×10^6 newtons per square meter (905 psi) was applied. After 30 minutes at these conditions the pressure was released and the mold was allowed to cool slowly to room temperature. The imidization time at 305° C (400° F) and dwell time at 315° C (600° F) for each of the small composites made are given in table II. The processing conditions for the larger panels, 7.62 by 25.4 centimeters (3 by 10 in.), differed from those previously described in the following respects. The stacked prepreg was placed between two three-ply layers of teflon-coated glass fabric bleeder cloth and a 4.1 kilogram mass (9 lb) was placed on the stack during imidization. After imidization, the layers of bleeder cloth were removed, the stack was placed between aluminum foil and molded at 3.85×10^6 newtons per square meter and 315° C (425 psi and 600° F).

Flexural tests were made on a three-point loading fixture with a fixed span of two inches. The specimens were 0.635 centimeters wide by 6.03 centimeters long (1/4 in. wide by 2-3/8 in. long). The nominal thicknesses of the small and large panels were 0.23 centimeter and 0.25 centimeter (0.090 and 0.100 in.), respectively. The rate of center loading was 0.127 centimeters per minute (0.05 in./min). The interlaminar shear tests were conducted at a constant span to thickness ratio of 5 using the interlaminar shear test fixture described by Hanson and Serafini.[7] The 315° C (600° F) flexural and interlaminar shear tests were performed in an environmental heating chamber. Load was applied to the specimens after a 15 minute soak at 315° C (600° F). Forced convection air ovens were used for the long-term isothermal exposures at 315° C (600° F). The air change rate was 100 cubic centimeters per minute (6.1 $in.^3$/min).

The data presented in table II are an average of two or more measurements at each condition. Six or more tests at each condition were averaged to give the data shown in figures 2 to 5, and 8 to 11.

3. RESULTS AND DISCUSSION

3.1 COMPOSITE SCREENING STUDY

In a prior investigation[4] we showed that the method of preparing composites from solutions of monomeric reactants provides composites with properties comparable to those of composites made from amide acid prepolymers. In addition, solutions of monomeric reactants offer several advantages over amide acid prepolymer solutions, most importantly low-boiling, relatively nontoxic alcohols such as methanol can be used as solvents instead of high-boiling, toxic solvents such as N,N-dimethylformamide.

In our previous work[4] we noted that certain composites made from monomer solutions containing BTDE had unexpectedly high thermooxidative stability. We therefore undertook a more detailed investigation to establish the optimum molar ratio of the reactants NE/MDA/BTDE.

Another objective of this investigation was to determine if the alicyclic content of the NE/MDA/PMDE system could be lowered further to improve its thermooxidative stability.

In our previous work[4] the number of diamines used in the prepreg solutions was limited to either 4,4'-methylenedianiline or 4,4'-thiodianiline. In this investigation six additional diamines were used in a composite screening study.

Also discussed is a comparison of composite properties from monomer solutions where the alicyclic content was kept constant, but the number of imide rings was varied.

The chemical composition, some curing parameters, and some properties of 19 various 1.27 by 6.35 centimeters (1/2 by 2-1/2 in.) composites are summarized in table II. The stoichiometry of the reactants was governed by the desired number of imide rings or by the desired percentage of alicyclic content. The term "formulated molecular weight" (FMW) is used as a convenience throughout this discussion. FMW is considered to be the average molecular weight of the imidized prepolymer that could have been formed if amide-acid prepolymers had been synthesized. For example, the structure of the imidized prepolymer resulting from monomeric solution 1 (table II) is expected to be similar to the structure shown in figure 1. For any given monomer combination, the molar ratio of 5-norbornene-2,3-dicarboxylic acid monomethyl ester/diamine/tetracarboxylic acid dimethyl ester was $2/(n + 1)/n$.

The dwell time (contact pressure time) of the composites in the heated mold was varied from 30 to 50 seconds. A decrease of dwell time tends to increase the amount of resin flow by minimizing the number of cross-links and chain extensions formed prior to application of pressure.

Samples 1 to 5 are chemically similar to the commercially available P13N resin. All of them, however, have a lower alicyclic content than P13N. Samples 1 to 3 possessed a combination of unusually high thermooxidative stability and high initial interlaminar shear at room temperature. They were therefore chosen for a more detailed study of mechanical properties after exposure at 315° C (600° F). Samples 4 and 5 were excluded from further study because of considerably inferior interlaminar shear values at room temperature.

Sample 6 has a composition equivalent to that of P10P prepolymer. Its properties were shown to be virtually identical with those of composites made from P10P. Samples 7 and 8 have the same chemical composition as sample 6, but differ in stoichiometry. Sample 7 was not selected for further study because its properties were not significantly superior to sample 6. Sample 8, having significantly lower interlaminar shear at room temperature and 315° C (600° F) was also excluded from further study.

The monomer combination used in samples 9 to 11 was selected to investigate the effect of increasing the number of imide linkages over that in the corresponding samples 1 to 3 while maintaining a constant alicyclic content. For example, sample 9 has the same alicyclic content as sample 1, but a higher number of imide linkages. The higher number of imide linkages is achieved by partial substitution of PMDE for BTDE. Theoretically this should give a correspondingly higher thermooxidative stability. Actually the results indicate that the thermooxidative stability of samples 9 to 11 is approximately equivalent to that of samples 1 to 3. Sample 9 was selected for further evaluation as representative of the NE/MDA/(1PMDE:1BTDE) monomer combination.

The monomer combinations in samples 12 to 19 (table II) and 20 to 24 (table III) were selected to determine the effect of seven additional diamine constituents on composite properties. These samples contained BTDE as the tetracarboxylic acid dimethyl ester component, with the exception of samples 16, 18, and 20 where PMDE was used in an effort to increase the number of imide linkages and therefore thermal stability. Sample 12 displayed excellent resin flow, but there was some blistering on the surface of the composite. Because the blisters could not be eliminated after numerous attempts, sample 12 was excluded from further study. Samples 13 to 19 were eliminated from advanced composite evaluation because of either a high composite weight loss or low initial interlaminar shear values. Composites from samples 20 to 24 (table III) had very poor consolidation, and

delaminated badly when subjected to mechanical testing. Therefore, it was impossible to obtain meaningful mechanical property data, and these samples were not subjected to further investigation.

3.2 ADVANCED COMPOSITE EVALUATION

Composite properties of samples 1 to 3 after exposure at 315° C (600° F) as a function of time are shown in figures 2 to 5. These tests were performed on 12-ply composites, 7.62 by 25.4 centimeters (3 by 10 in.). For comparison purposes, composite data for sample 6 are also presented in figures 2 to 5. Sample 6 is chemically equivalent to the composites prepared from the P10P prepolymer developed by Burns, et al.,[3] which had yielded the best thermooxidative stability for addition-type polyimides up to the present investigation.

Figure 2 shows that the composite weight loss for samples 1 to 3 was considerably lower than that of sample 6. It is difficult to attach too much significance to the weight loss differences among samples 1 to 3 because of the vagaries of isothermal analysis. However, it is significant to note that the average percent weight loss (11.2 percent) for samples 1 to 3 after 600 hours was 39 percent lower than the weight loss for sample 6.

Figures 3 to 5 show the variation of mechanical properties for samples 1 to 3 and 6 after exposure at 315° C (600° F) as a function of exposure time. Also presented are the room temperature and short time 315° C (600° F) properties.

The interlaminar shear strength is shown in figure 3. The range of the room temperature values is 95×10^6 newtons per square meter to 123×10^6 newtons per square meter (13 800 psi to 17 800 psi). These values are somewhat higher than those previously reported[7] for A-type polyimide/HTS fiber composites. There is a considerable drop in the interlaminar shear strength when the composites are tested at 315° C (600° F), to as low as 34.5 newtons per square meter (5000 psi). There was a greater decrease for samples 1 to 3 than for sample 6. The interlaminar shear strength decrease for sample 6 is nearly identical to that reported by Hanson and Serafini.[7]

It appears that composite samples 1 to 3 underwent a post-cure on exposure in air at 315° C (600° F), since the interlaminar shear strength increased during exposure, whereas that of sample 6 decreased with time. The important fact to note is that the interlaminar shear strength of samples 1 to 3 remained nearly constant from 100 to 600 hours. The strength after 600 hours for samples 1 to 3 averaged approximately 45×10^6 newtons per square meter (6500 psi), compared to 33×10^6 newtons per square meter (4800 psi) for sample 6, representing a 35 percent increase. The data for samples 1 to 3 represent the best interlaminar shear retention for A-type polyimide/HTS fiber composites reported to date. The interlaminar shear strength of sample 1 increased to 48.5×10^6 newtons per square meter (7000 psi) after 200 hours of exposure and remained constant up to 600 hours of exposure. It appears that the interlaminar shear strength would have remained constant for a considerably longer time if the exposure time had been extended. The interlaminar shear strengths of samples 2 and 3 began to decrease after reaching maximum values after 200 hours to approximately 43×10^6 newtons per square meter (6200 psi) after 600 hours. These results are somewhat contrary to the expected improvement in thermooxidative stability and mechanical properties for samples 2 and 3, resulting from the higher number of imide rings and lower alicyclic content. This discrepancy could possibly be attributed to slightly poorer resin flow during the final curing step for samples 2 and 3. In view of these results we feel that the stoichiometry of reactants used in sample 1 is preferred.

The flexural strength results are shown in figure 4. Many of the comments presented in the discussion of interlaminar shear strength are also applicable here. For example, a post-cure effect is also evident for composite samples 1 to 3. The flexural strength values for sample 3 are lower than those for samples 1 and 2 throughout the 600 hour exposure. This could again be attributed to minor differences in resin flow during processing. It is important to note, however, that after 600 hours of exposure the flexural strength of samples 1 and 2 was nearly twice that of sample 6.

The variation of the flexural modulus of elasticity as a function of exposure time is shown in figure 5. Here, too, a post-cure effect was observed. The modulus values for samples 1 to 3 did not differ appreciably, and remained essentially constant from 100 to 600 hours. On the other hand, the modulus of sample 6 showed a marked decrease after 300 hours.

Photomicrographs of a cross-section of composite sample 1, before and after exposure, are shown in figure 6. There is no evidence of voids in the composite as a result of fabrication. After exposure at 315° C (600° F) for 600 hours, the composite shows an extremely small number of voids. This indicates that the original void-free composite was very resistant to oxidative degradation that might occur by a diffusion mechanism. Any degradation that did occur, took place on the surface of the composite. The absence of internal voids after exposure also indicates that the composite is very resistant to thermal decomposition.

Figure 7 shows the photomicrographs of

composite samples 2 and 3 before exposure at 315° C (600° F). The photomicrographs show the presence of a small number of voids in both cases. These might be responsible for the slightly inferior mechanical property retention of samples 2 and 3, compared with sample 1.

To sum up the results of this portion of the advanced composite evaluation we conclude that the stoichiometry used in sample 1 provided composites having the best combination of processability and thermomechanical properties. Sample 3, which had the largest number of imide rings and lowest alicyclic content, would be expected to exhibit the best performance. However, its performance was not as good as that of composite sample 1, which had a fewer number of imide rings. We attribute this finding to the better resin flow and processability obtained using the stoichiometry of sample 1. However, each of the composite samples 1 to 3, containing BTDE as the tetracarboxylic acid component, yielded significantly better property retention than sample 6 (containing PMDE), which had given the best thermomechanical performance up to the present investigation.[4]

The remaining sample selected for advanced composite evaluation was sample 9. In sample 9, 50 mole percent of BTDE were replaced with PMDE, because theoretically PMDE should be more stable thermooxidatively than BTDE. In addition, sample 9 possessed the same alicyclic content as sample 1. The photomicrograph of sample 9 was similar to that of sample 1 (figure 6). The effects of long-term exposure at 315° C (600° F) on the composite properties of sample 9 are shown in figures 8 to 11. For comparison, the properties of sample 1 (containing BTDE) and sample 6 (containing PMDE) are included.

The composite weight loss data presented in figure 8 show that the weight loss curve for sample 9 is almost identical with that for sample 1. It can be seen that partial inclusion of the more stable PMDE did not improve the thermooxidative stability of sample 9 over that of sample 1.

The interlaminar shear strength values are shown in figure 9. The shear strength retention of sample 9 was inferior to that of sample 1. There was not much difference in the interlaminar shear strength of samples 1 and 9 for 200 hours at 315° C (600° F). However, the shear strength of sample 9 began to show a decrease after 200 hours of exposure, and became nearly identical with that of sample 6 after 600 hours (35 percent lower than the shear strength of sample 1).

The variation of flexural strength as a function of exposure time is shown in figure 10. Again it is apparent that the flexural strength of sample 9 was considerably lower than that of sample 1, and only slightly higher than that of sample 6. After exposure for 600 hours the flexural strength of sample 9 was 30 percent lower than that of sample 1.

The variation of the flexural modulus, shown in figure 11 was approximately the same for all three samples.

In summary, the partial replacement of BTDE with PMDE did not significantly improve the mechanical properties of sample 9 over those of sample 6, even though sample 9 exhibited excellent weight retention at 315° C (600° F). These results indicate that one cannot rely exclusively on isothermal weight loss data for prediction of composite performance.

4. CONCLUSIONS

Based on the results of the present investigation, the following conclusions can be drawn:

a. For addition-type polyimide/graphite fiber composites prepared via the monomeric reactants approach, the most suitable aromatic diamine was found to be 4,4'-methylenedianiline (MDA).

b. By replacing the dimethyl ester of pyromellitic acid (PMDE) with the dimethyl ester of 3,3'4,4'-benzophenonetetracarboxylic acid (BTDE), it was possible to fabricate addition-type polyimide/graphite fiber composites with better resin flow and improved mechanical properties and thermooxidative stability in air at 315° C (600° F) after 600 hours than composites containing PMDE.

c. The monomer composition 5-norbornene-2,3-dicarboxylic acid monomethyl ester (NE) with MDA and BTDE at three different stoichiometric ratios yielded composites that possessed long-term mechanical properties and thermooxidative stability superior to those of P10P composites. The panels fabricated from the NE/MDA/BTDE formulation at a molar ratio of 2/3.09/2.09 (sample 1) gave the best overall mechanical properties of all panels studied. After 600 hours' exposure in air at 315° C (600° F), the interlaminar shear strength of sample 1 was 45 percent higher than that of P10P composites, and the flexural strength of sample 1 was 75 percent higher than that of P10P composites.

REFERENCES

1. Lubowitz, H. R.: Polyimide Polymers. U.S. Patent 3,528,590, Sept. 15, 1970.

2. Burns, E. A.; Lubowitz, H. R.; and Jones, J. F.: Investigation of Resin Systems for Improved Ablative Materials. Rep. TRW-05937-6019-RO-00, TRW Systems Group, (NASA CR-72460), Oct. 1, 1968.

3. Burns, E. A.; Jones, R. J.; Vaughan, R. W.; and Kendrick, W. P.: Thermally Stable Laminating Resins. Rep. TRW-11926-6013-RO-00, TRW Systems Group (NASA CR-72633), Jan. 17, 1970.

4. Serafini, Tito T.; Delvigs, Peter; and Lightsey, George R.: Thermally Stable Polyimides from Solutions of Monomeric Reactants. NASA TN D-6611, 1972.

5. Walton, H. M.: Potential Antimicrobial Agents. I. Alkyl 4-Oxo-2-alkenoates. J. Organic Chem., vol. 22, no. 3, Mar. 1957, pp. 308-312.

6. Bell, Vernon L.; and Jewell, Robert A.: Synthesis and Properties of Polyimidazopyrrolones. J. Polym. Sci., Pt. A-1, vol. 5, no. 12, 1967, pp. 3043-3060.

7. Hanson, M. P.; and Serafini, T. T.: Effects of Thermal and Environmental Exposure on the Mechanical Properties of Graphite/Polyimide Composites. NASA TN D-6604, 1971.

TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

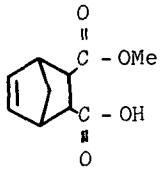
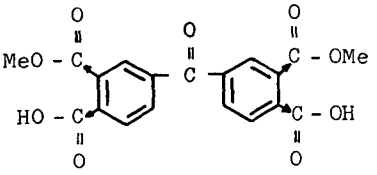
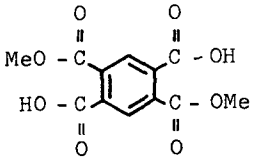
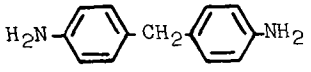
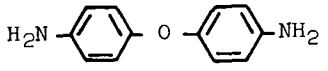
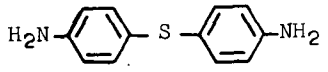
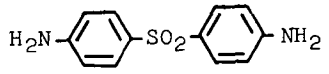
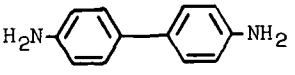
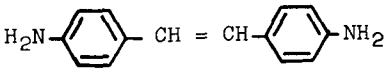
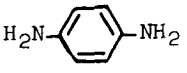
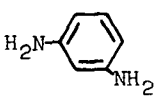
Monomer structure and name		Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid	BTDE
	2,5-Dicarbomethoxyterephthalic acid	PMDE
	4,4'-Methylenedianiline	MDA
	4,4'-Oxydianiline	ODA
	4,4'-Thiodianiline	TDA
	4,4'-Sulfonyldianiline	SDA
	Benzidine	BZD
	4,4'-Diaminostilbene	DAS
	p-Phenylenediamine	PPDA
	m-Phenylenediamine	MPDA

TABLE II. - PROPERTIES OF VARIOUS 1.27 BY 6.35 CM (1/2 BY 2-1/2 IN.)

POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES

Sample number	Monomeric solution composition	n	FMW	Processing conditions: Imidization time at 205° C (400° F), hr	Processing conditions: Dwell time at 315° C (600° F), sec	Laminate properties: Interlaminar shear at 24° C (75° F) N/m^2	Interlaminar shear at 24° C (75° F) ksi	Interlaminar shear at 315° C (600° F) N/m^2	Interlaminar shear at 315° C (600° F) ksi	Composite weight loss, percent[a]
[b]1	NE/MDA/BTDE	2.087	1500	3	50	105.5×10^6	15.3	41.4×10^6	6.0	9.5
2		2.603	1750	3	40	99.3	14.4	37.9	5.5	9.8
3		2.913	1900	3	40	103.4	15.0	35.2	5.1	10.0
4		3.120	2000	3	30	67.6	9.8	31.7	4.6	11.4
5		5.186	3000	3	30	56.5	8.2	35.2	5.1	28.0
[b]6	NE/MDA/PMDE	1.342	1000	2	50	74.5	10.8	42.7	6.2	17.6
7		1.868	1200	2	40	84.8	12.3	42.7	6.2	17.9
8		2.658	1500	2	30	42.1	6.1	20.0	2.9	20.8
9	NE/MDA/ (1BTDE:1PMDE)	2.338	1500	2	50	98.6	14.3	42.7	6.2	10.6
10		2.917	1750	3	40	93.8	13.6	37.9	5.5	8.6
11		3.264	1900	3	40	86.9	12.6	31.0	4.5	10.9
12	NE/MPDA/BTDE	2.793	1500	3	40	87.6	12.7	31.0	4.5	17.3
13		3.426	1750	4	40	56.3	8.2	31.0	4.5	16.3
14	NE/ODA/BTDE[c]	2.074	1500	3	40	62.1	9.0	33.1	4.8	24.2
15		2.897	1900	3	30	69.0	10.0	30.3	4.4	19.1
16	NE/TDA/PMDE	2.492	1500	2	50	51.0	7.4	25.5	3.7	22.6
17	NE/TDA/BTDE	1.975	1500	3	40	46.9	6.8	25.5	3.7	14.6
18	NE/SDA/PMDE[c]	1.070	1000	2	50	23.4	3.4	17.9	2.6	15.6
19	NE/SDA/BTDE[c]	1.000	1074	2	50	31.7	4.6	17.9	2.6	15.5

[a]After 600 hours in air at 315° C (600° F).

[b]Data taken from reference 4.

[c]Solvent - 1-methyl-2-pyrrolidinone.

TABLE III. - UNSUCCESSFUL MONOMER COMBINATIONS

Sample number	Monomeric solution composition	n	FMW
[a]20	NE/PPDA/PMDE	2.069	1000
21	NE/PPDA/BTDE	1.000	794
22	NE/BZD/BTDE	2.179	1500
[a]23	NE/DAS/BTDE	1.004	1000
[a]24	NE/DAS/BTDE	2.012	1500

[a]Solvent - 1-methyl-2-pyrrolidinone.

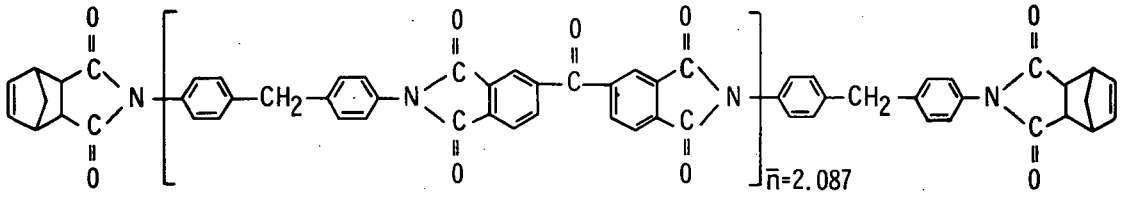


Figure 1. - Imidized prepolymer from NE/MDA/BTDE, FMW=1500.

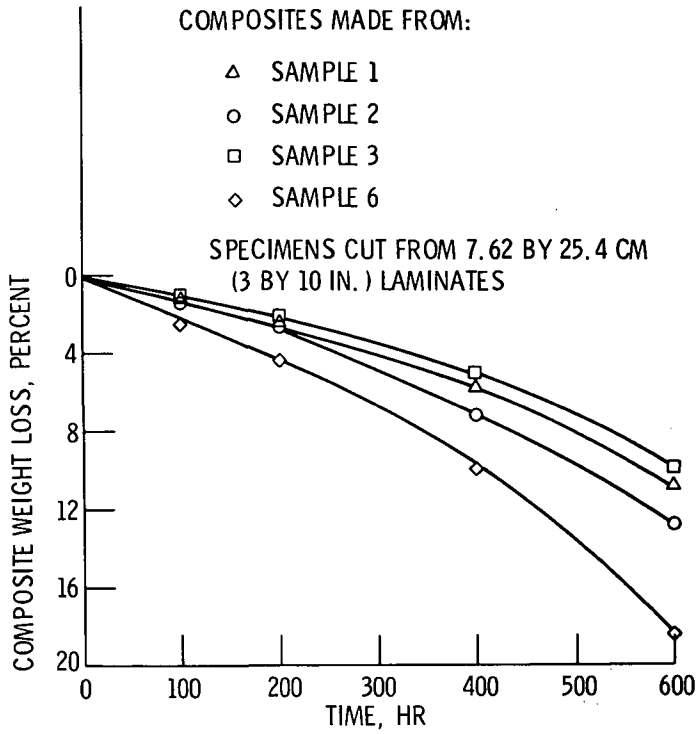


Figure 2. - Percent weight loss of polyimide/HTS graphite fiber composites exposed in air at 315° C (600° F).

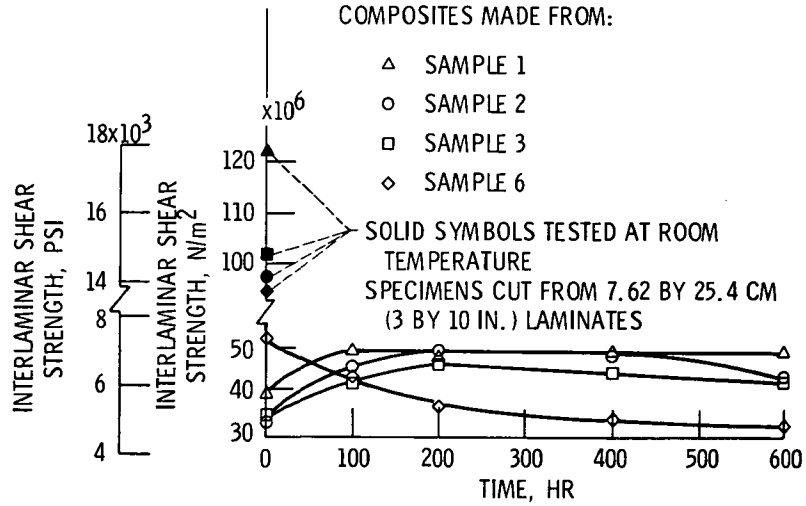


Figure 3. - Interlaminar shear strength of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).

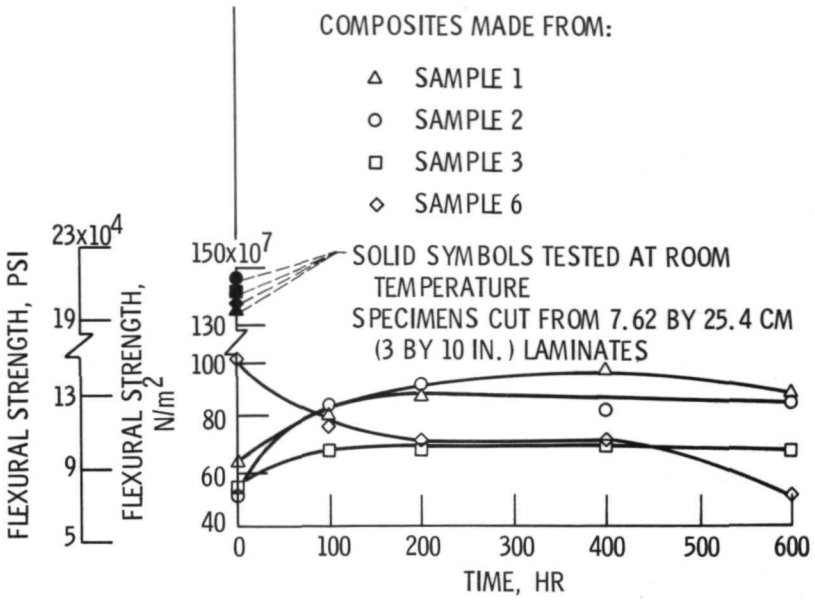


Figure 4. - Flexural strength of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).

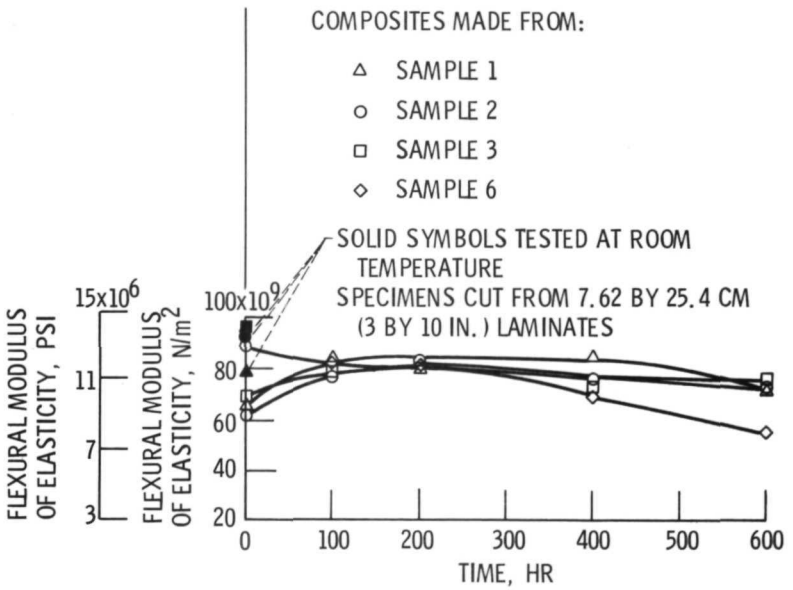
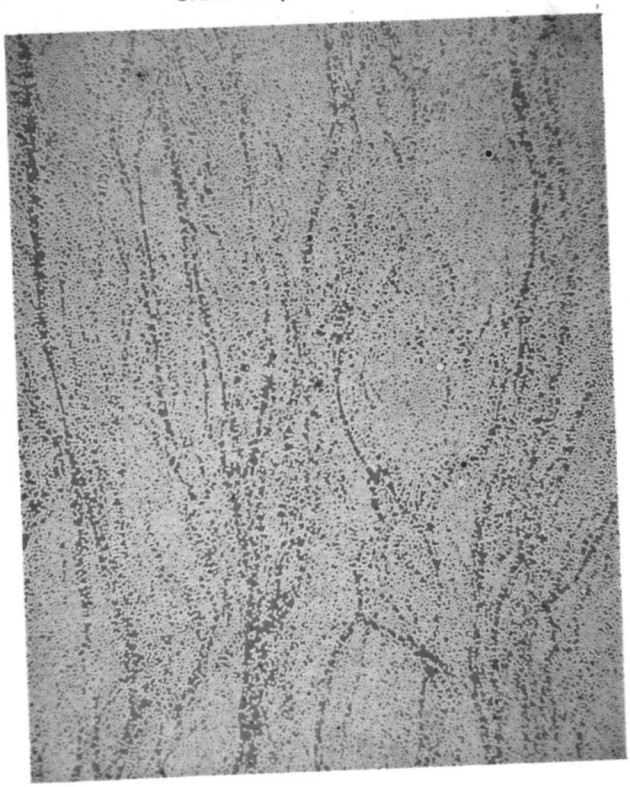


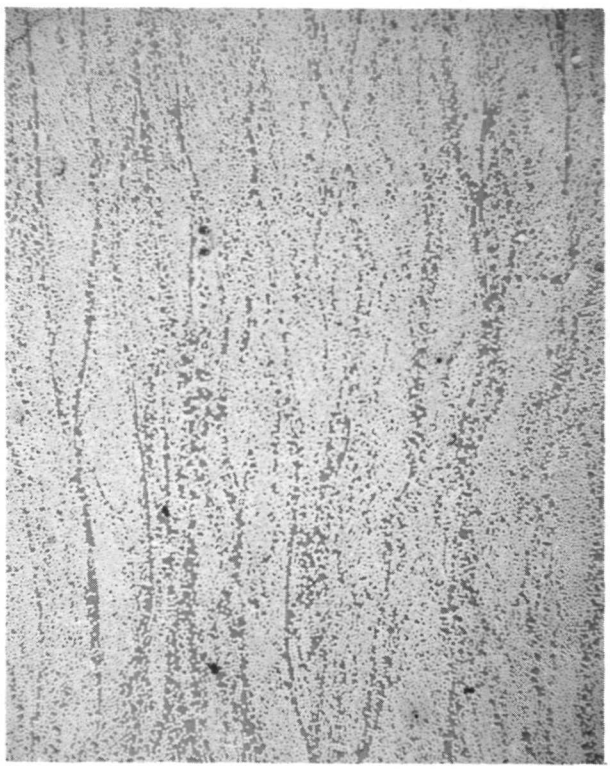
Figure 5. - Flexural modulus of elasticity of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).

SAMPLE 1, UNEXPOSED.

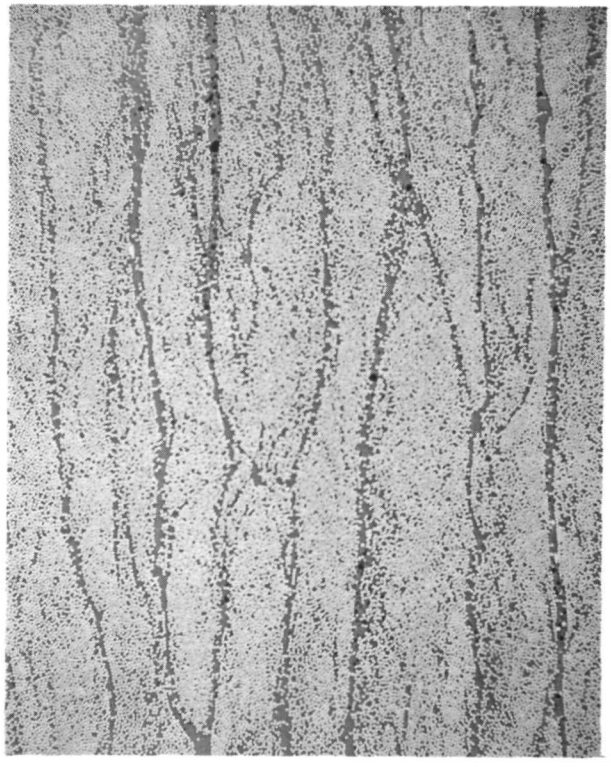


SAMPLE 1, EXPOSED.

Figure 6. - Photomicrographs of polyimide/HTS graphite fiber composites before and after exposure in air at 315° C (600° F) for 600 hours. X50.



SAMPLE 2.



SAMPLE 3.

Figure 7. - Photomicrographs of unexposed polyimide/HTS graphite fiber composites. X50.

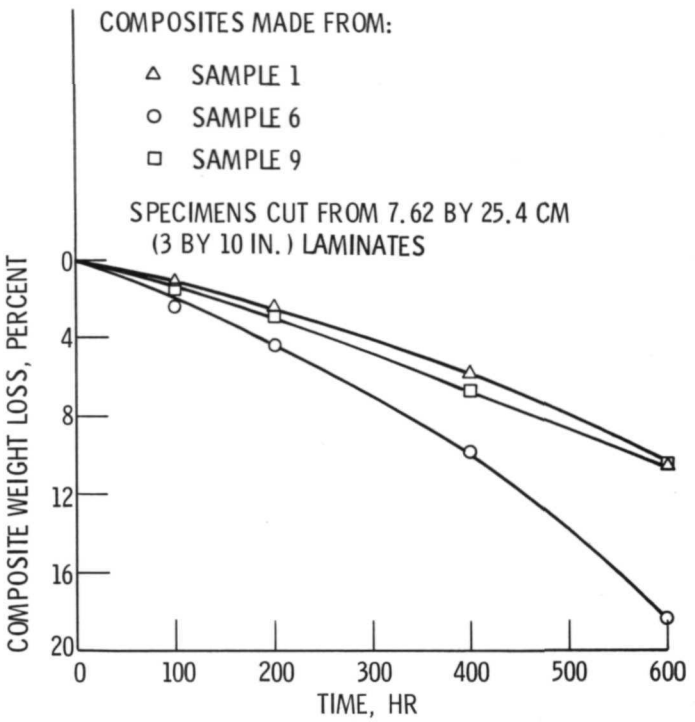


Figure 8. - Percent weight loss of polyimide/HTS graphite fiber composites exposed in air at 315° C (600° F).

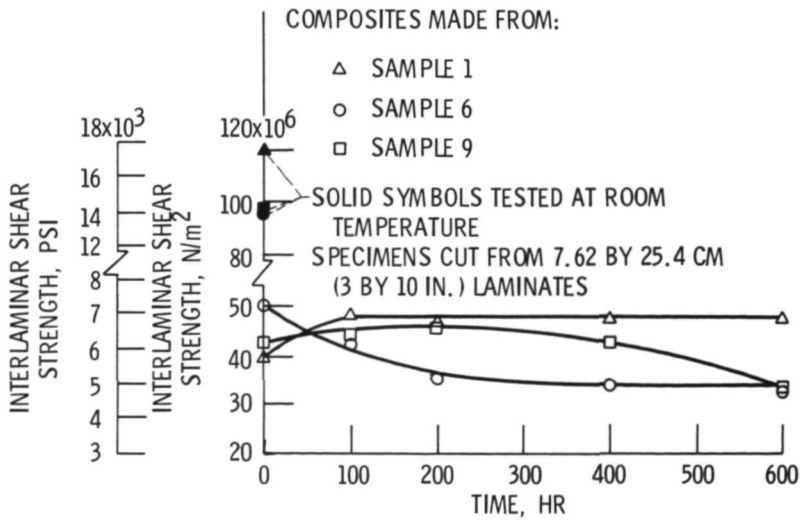


Figure 9. - Interlaminar shear strength of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).

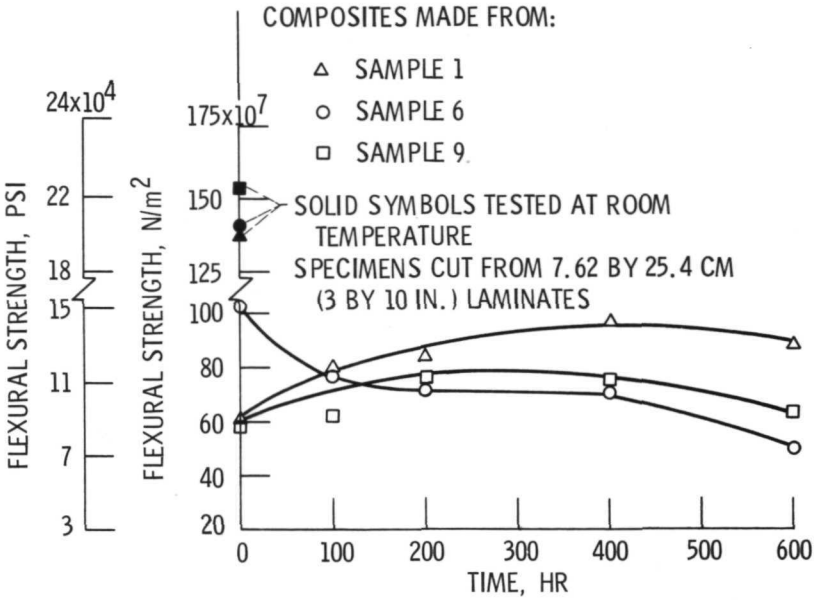


Figure 10. - Flexural strength of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).

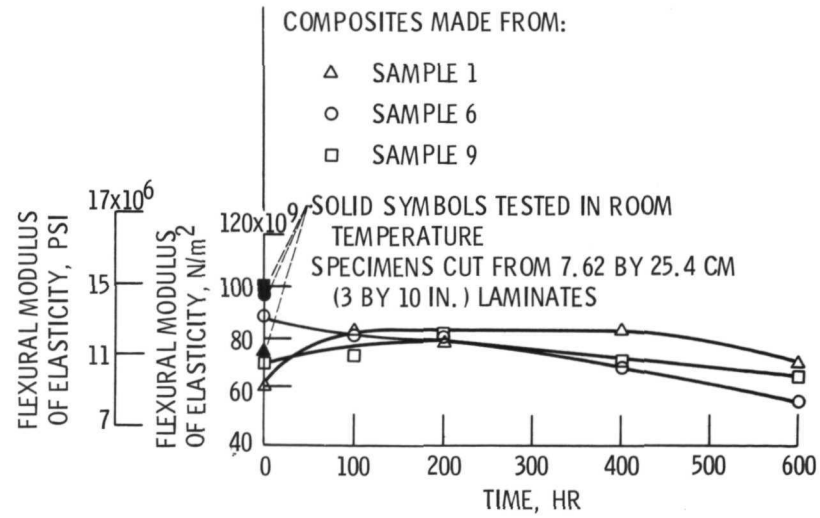


Figure 11. - Flexural modulus of elasticity of polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F).